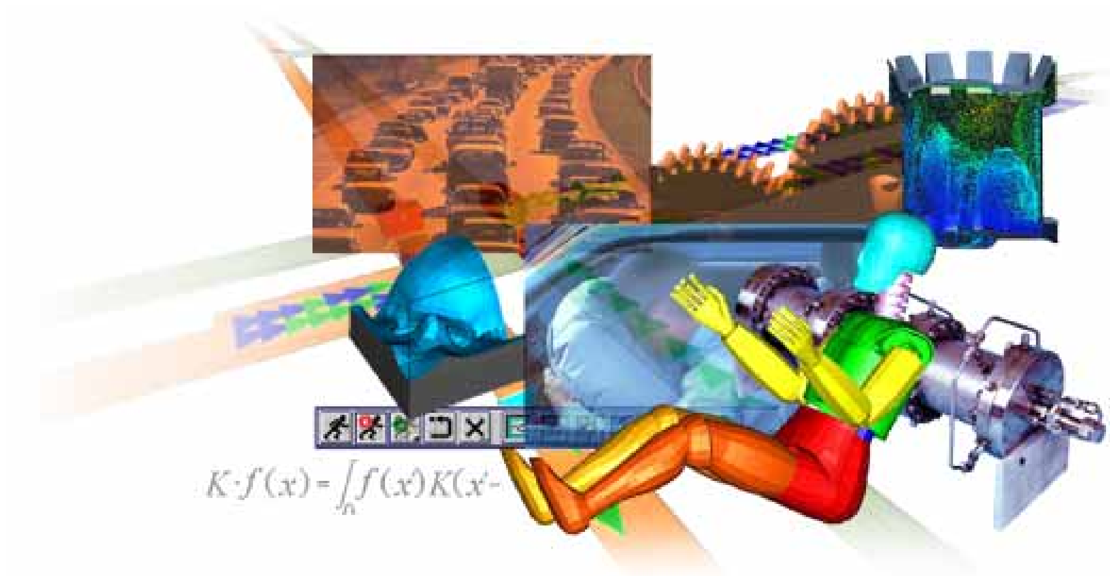
Exhaust Gas Sensors

David E. Watkins

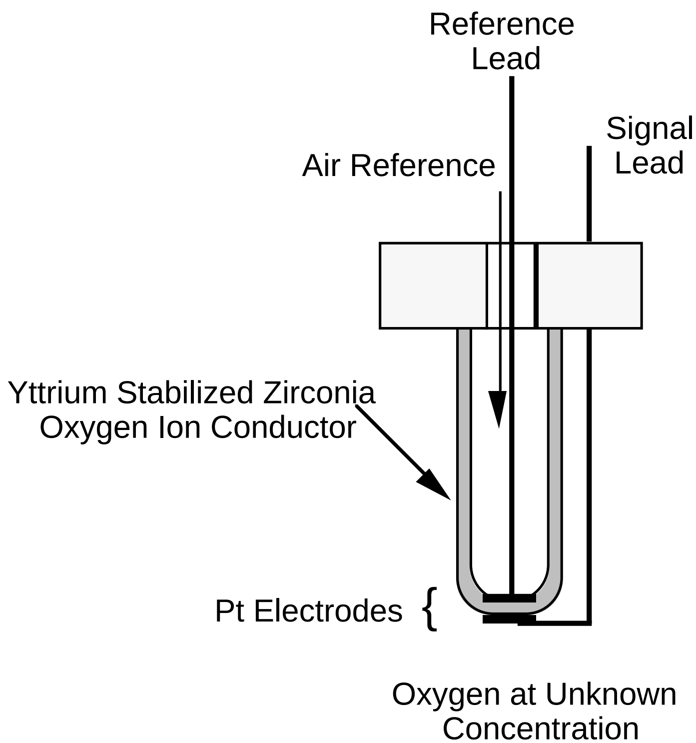
Electronics Research Group, Materials Science and Technology Division

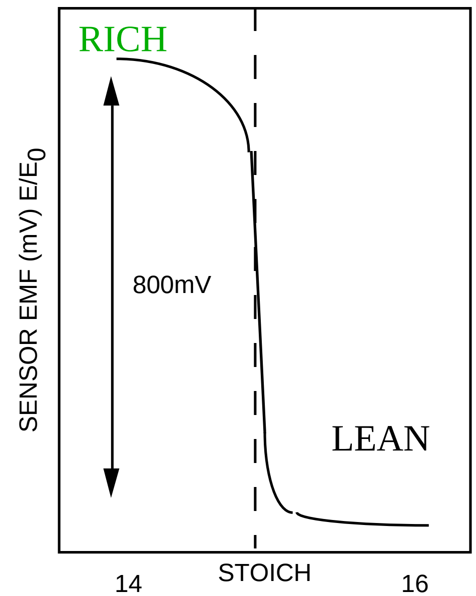
E-Mail: watkins@lanl.gov
Phone: 505-667-6832
Fax: 505-665-4292



Current Generation ZrO_2 Oxygen Sensors

for Closed-loop Active Combustion Control

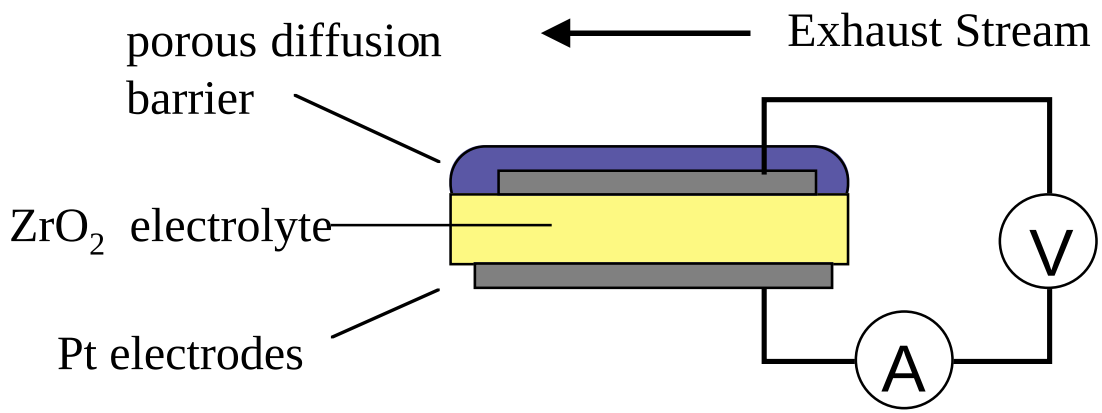


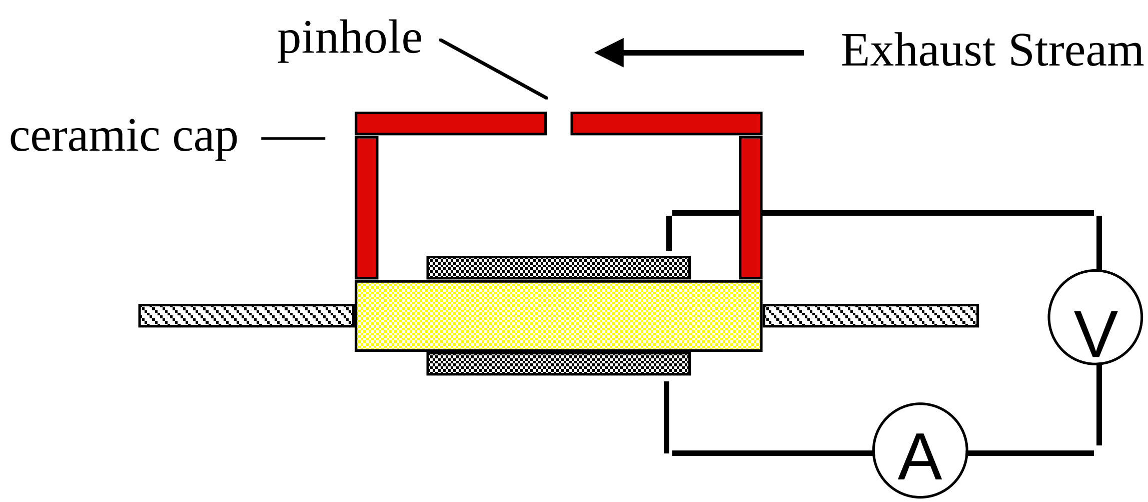


$$E = \frac{RT}{4F} \ln\left(\frac{P'_{O_2}}{P''_{O_2}}\right)$$

Current Amperometric Oxygen Sensor Technology for "Lean-Burn" Engines

- **Two limiting current oxygen sensor configurations have been reported in the literature for ULEV applications:**
  - **utilize physical diffusion barriers to produce a limiting current response under electrochemical O_2 pumping,**
  - **porous films subject to particulate clogging,**
  - **pinholes are expensive to manufacture & gas-tight seals are required.**





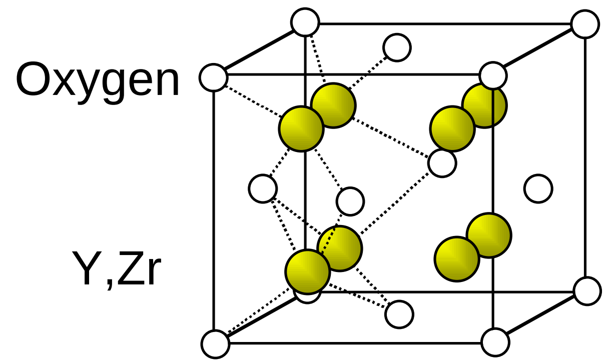
Solid Oxide Mixed Ionic/Electronic Conducting Ceramics

- **Oxygen non-stoichiometric structures such as perovskites and fluorites can tolerate missing ions**
  - **e.g. Doping a tri- or di-valent cation onto the zirconia site will introduce oxygen ion vacancies**

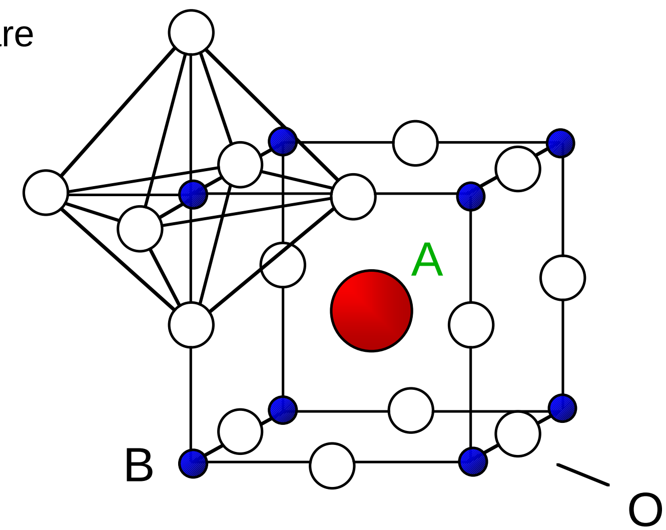
$$\left.\begin{array}{ll} Y^{+3}{}_{x}Zr^{+4}{}_{1-x}O_{2-x/2} & (x \leq 0.25) \\ Ca^{+2}{}_{x}Zr^{+4}{}_{1-x}O_{2-x} & (x \leq 0.15) \end{array}\right\}$$

Oxygen vacancies are mobile at elevated temperature.

- **Oxygen ion conductivity (oxygen ion vacancy concentration) as well as electronic (p and n-type) conductivity can be controlled by chemical substitution on the A and B cation sites in the perovskite structure**
  - **e.g. $La_{1-x}Sr_xCoO_3$, $La_{1-x}Sr_xMnO_3$**

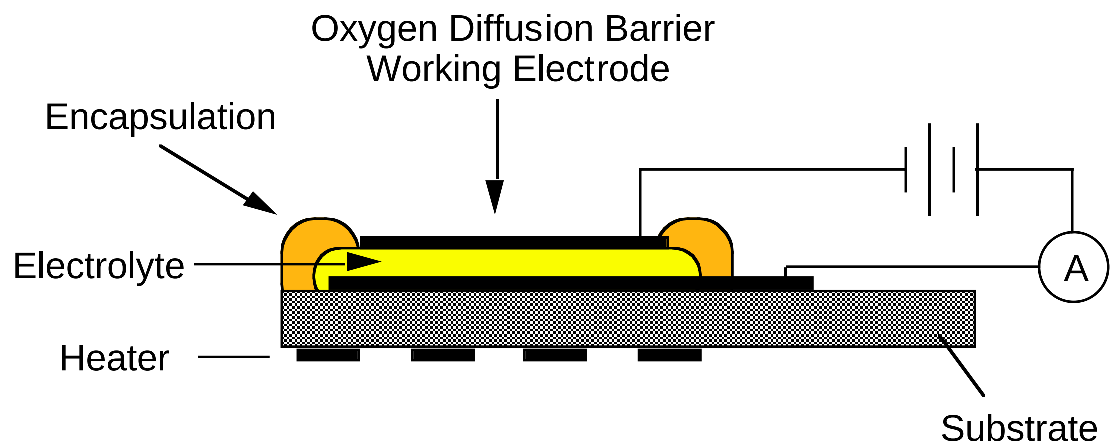


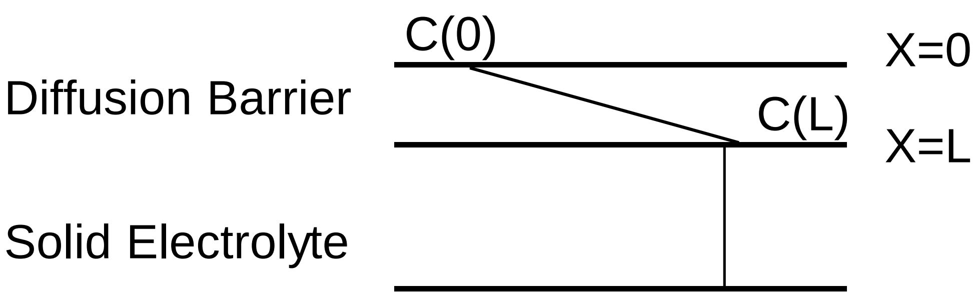
Fluorite Structure



ABO_3 Perovskite

LANL Limiting Current Oxygen Sensor





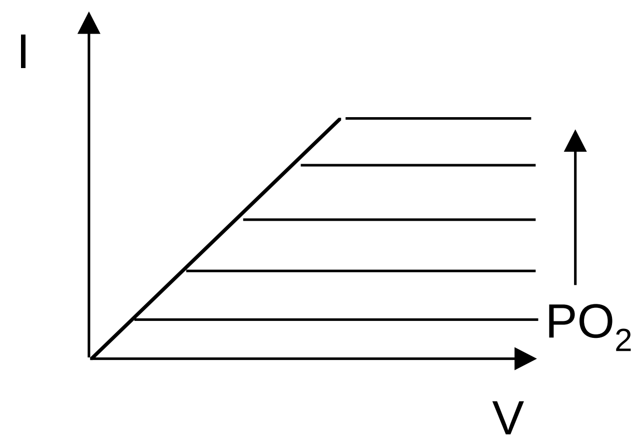
$$I_l = \frac{4F\, D_{O_2} S}{L} C_{O_2}(0)$$

Fick’s First Law: the flux of oxygen ions pumped through an oxygen-ion conducting electrolyte is proportional to the diffusion coefficient of the metal oxide diffusion barrier applied to the electrolyte and the concentration of oxygen above the barrier.

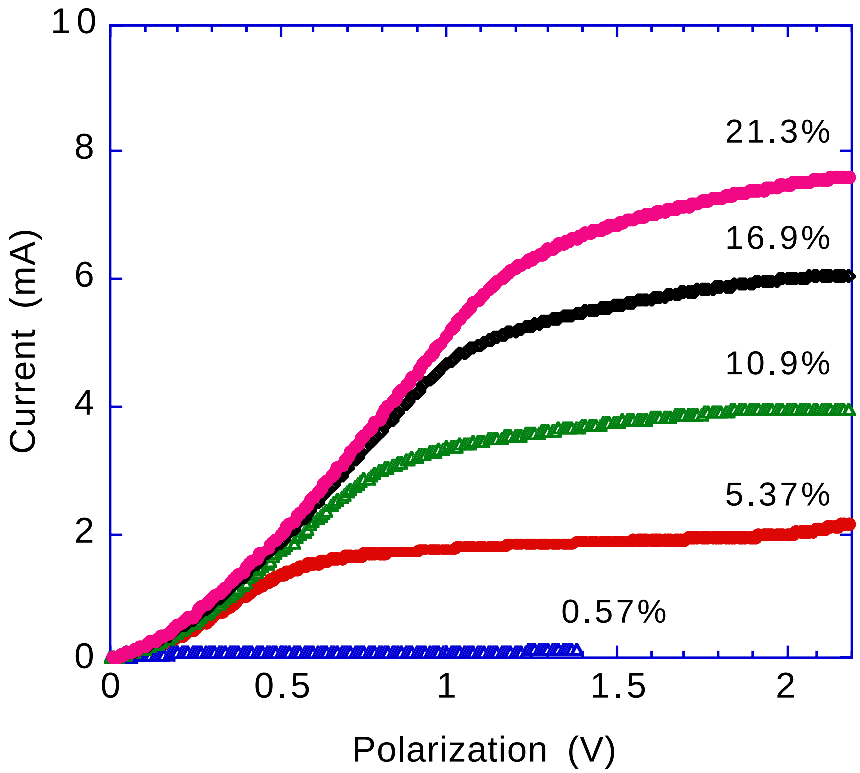
LANL Limiting Current Oxygen Sensor

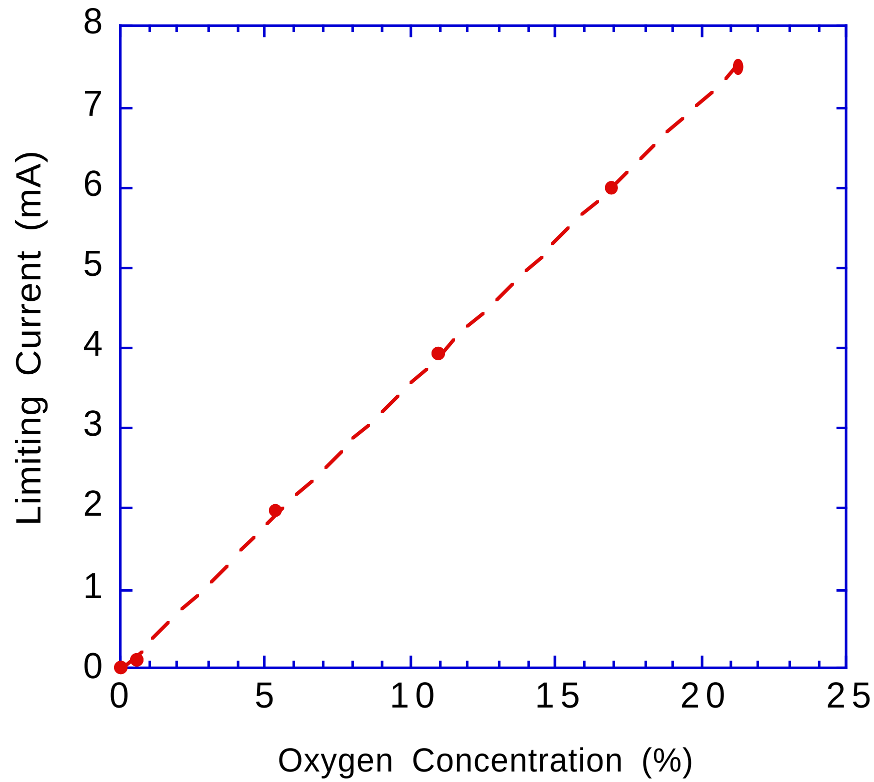
- **The LANL linear-response oxygen sensor based on perovskite or doped YSZ oxygen diffusion barriers applied to a zirconia oxygen ion pump.**
  - **The rate of oxygen transport through the chemical diffusion barrier is governed by the effective diffusion coefficient of lattice oxygen in the electronic metal oxide.**
  - **The effective oxygen diffusion coefficient is controlled by materials chemistry and geometry.**
  - **Technology lends itself to low cost manufacturing techniques.**

The result is a device that exhibits limiting current plateaus linearly proportional to PO_2 (right)



LANL Limiting Current Oxygen Sensor - performance





Dynamometer Testing of Sensors

Thick Tb-Doped YSZ Diffusion Barrier Films

- **LANL has demonstrated linear current oxygen sensors that utilize several types of fluorite and perovskite transition metal oxides chemically modified to exhibit high oxygen ion and electron conductivities for application as oxygen ion diffusion barriers. These advanced materials were tested in exhaust gas environments:**
  - "Engine out" exhaust from a carbureted 5.7 litre Chevrolet engine without catalyst upstream of sample test station.
  - Samples were shrouded from direct impingement of particulates using lambda oxygen sensor-type packaging.
  - Engine was operated at lambda = 1.05 $\pm$ 0.005 for 150 hours in three 50 hour increments with 2-3 hours total operation under rich conditions.
  - premium fuel with 300 ppm sulfur and 4 mg Lead/gal added
    - $T_{inlet} = 800°C$; $T_{outlet} = 750°C$

Sensors for Industrial Combustion Control Applications

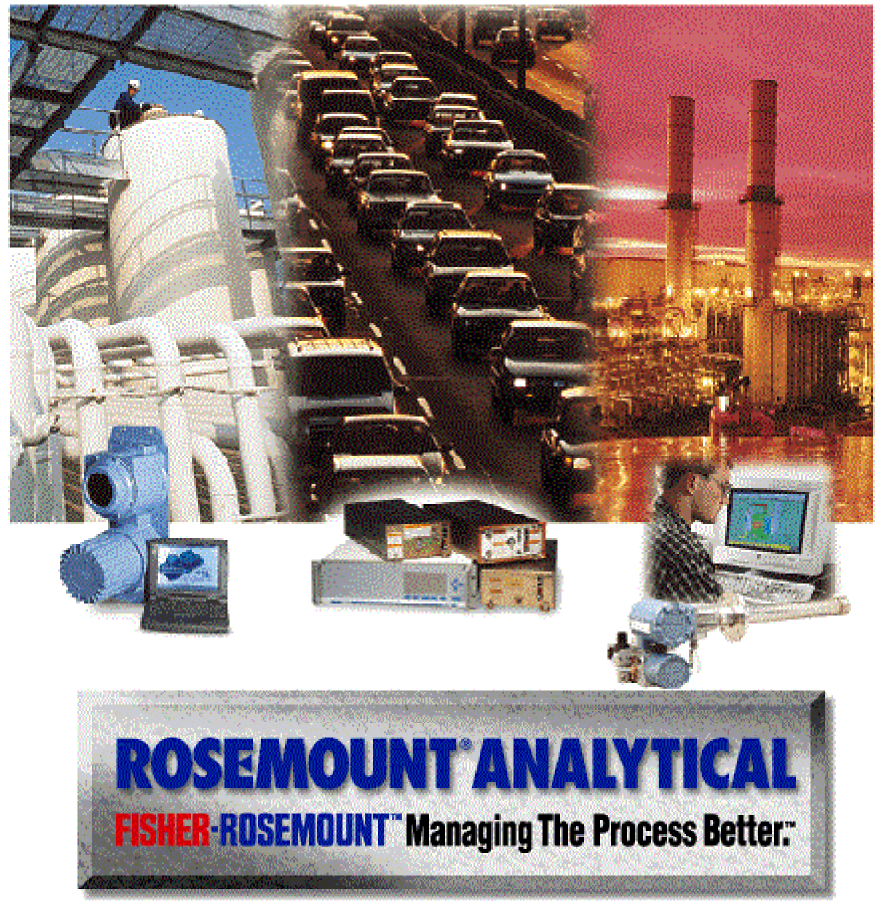
- The ZrO_2 oxygen analyzer is now the industry standard for controlling the fuel/air ratio of large boilers to achieve an optimum heat rate efficiency
  - 8 to 10% oxygen in exhaust without sensor
  - 4% with oxygen sensor, ~5% energy savings
  - 3% with *good* oxygen sensor, 1% additional energy savings
  - 2.5% with good oxygen sensor and HC/CO gas sensor, ~ 0.5% additional energy savings
- Problems with current zirconia technology:
  - Users of this technology face two sensor degradation mechanisms that limit successful long term operation of *insitu* analyzer probes (Sulfur and high temperature degradation)
  - Oxygen sensors measure equilibrium oxygen concentration

Demonstrated Application: Industrial Boiler Control

- **The electrochemical sensor technology developed at LANL has been applied to active combustion control of industrial boilers.**
  - **Typical sulfur levels in coal and crude oil far exceed the levels of sulfur found in refined gasoline.**
- **LANL development of sulfur resistant oxygen sensors and lifetime testing in real-world, high sulfur environments (in excess of 10% SO_2) serve to validate technology and provide valuable fundamental electrochemical and materials data that can be used to improve automotive sensors.**

LANL Collaboration with Fisher/Rosemount Analytical

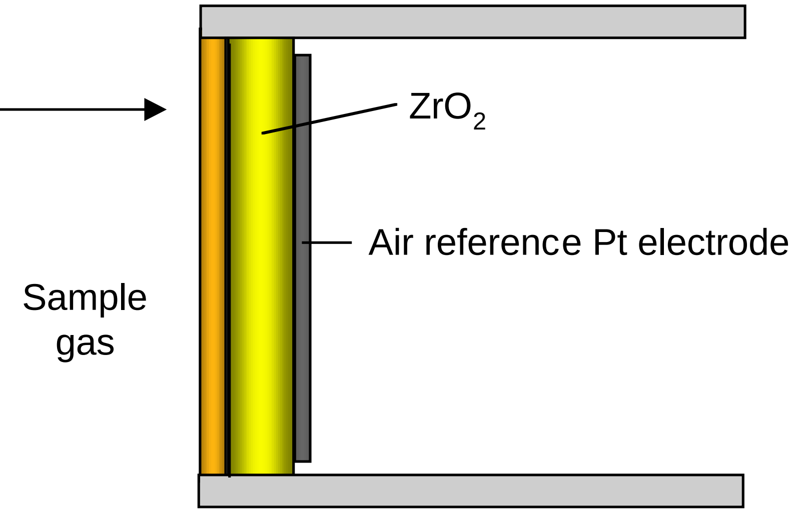
Rosemount Analytical is the world's largest supplier of analytical instruments and systems for process gas analysis, combustion analysis and control, and emissions monitoring. **We have entered into a cooperative research agreement with Rosemount Analytical Corporation to develop new oxygen and total combustibles sensors that are capable of surviving high sulfur environments without degradation.**



High Temperature, Sulfur Resistant Oxygen Sensors Based on Tb-doped YSZ

Nernstian response oxygen sensors utilizing $Tb_yY_xZr_{1-x-y}O_{2-\partial}$ in place of Pt

LANL Sulfur Resistant Cell



Stainless steel tube surrounded by electric heater

- **Our oxygen sensor will work on boilers that present sensor technology can't control**
  - **improved corrosion resistance (>12 months continuous operation in high sulfur environment)**
  - **higher possible operating temperature**

Technical Benefits of LANL Sensor Technology

- **Based on proven electrochemical sensor technology:**
  - **Utilizes yttria stabilized zirconia oxygen ion-conductors.**
  - **Potentiometric sensors utilizing these materials have been used in automobiles with active feedback control for over twenty years.**
- **Uses advanced high temperature refractory metal oxide materials:**
  - **Chemical and physical stability of these materials in the automotive exhaust environment is tailored by controlling the crystal chemistry through chemical substitution.**
  - **Sensor technology can be low-cost:**
  - **Materials less expensive than current technology**
  - **Amenable to low cost manufacturing techniques used by the automotive community.**

Present State-of-Development

- **Metal oxide electrode materials have been tested in realistic conditions:**
  - **dyno tested in engine-out conditions**
  - **tested in high sulfur boiler exhaust environments.**
- **Commercial versions of the LANL sulfur resistant oxygen sensor will soon be available in the marketplace.**
- **LANL linear current or “lean-burn” oxygen sensors using a variety of metal oxide oxygen diffusion barriers have been tested in laboratory conditions.**
- **Additional testing in engine out conditions to evaluate and optimize performance (response time, sensitivity, resistance to particulate impingement, temperature response, and cross sensitivity to hydrocarbons or CO).**

Industrial Research Partners

- Industrial partners can provide valuable expertise in the area of testing LANL sensors under real-world conditions.
  - dyno testing, thermal shock testing, evaluation of cross-sensitivity to CO and HCs
- Industry has experience to aid in researching important considerations such as:
  - Sensor response modeling
  - Design and development of device packaging
  - Design and development of support electronics
  - Integration of new sensor technologies with low-cost and high-volume manufacturing techniques
- Partnering to co-develop new electrochemical sensors (NOx)

Conclusion

- **LANL seeks industrial partnerships to exploit novel electrochemical sensors**
  - **Oxygen (linear or nernstien response, chemically stable in harsh environments, compatible with high temperature operation)**
  - **Hydrocarbon and CO sensors**
  - **NOx and SOx sensors**